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PITTSBURGH COKE & CHEMICAL COMPANY

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CONFIDENTIAL

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CONTRACT NO: DA-18-108-CML-5839

PERIOD: JUNE 1 - 30, 1956

PITTSBURGH COKE & CHEMICAL COMPANY

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ABSTRACT:

ASC Whetlerite Ageing:

Further work was done on the reversible ageing commented on previously.
CK life on a sample of ASC plant Whetlerite at 80-80 and 6 cm. bed depth was
237 minutes. After ageing at 80% RH (room temperature equilibration) and
80°C. for 24 hours, the CK life at 80-80 was 56 min. Drying this material
at 105°C. and 150°C. for 3 hours gave 154 minute life in each case. Moving
air at 28% RH over the Whetlerite for 18 hours at room temperature and
re-equilibrating at 80% RH gave a life of 129 minutes. Thus very little
activation energy is needed for reversing the state of the Whetlerite and
one would guess we are dealing with a physical change. The amount of water
present is essentially the same in all cases before testing. A simple
redistribution of the copper chromate would be one answer. Even long equili-
bration at 80% RH where no water evaporation can occur leads to a slow rise
in CK life. (Aged life 37 min. equilibrated 24 hours at 80% RH 40 min.,
50 hrs. 45 min., and 120 hrs. 51 min.)

As the Whetlerite CK life is further aged by longer treatment at 80°C.
CK life is reduced to that of raw carbon. On drying, CK lives are consider-
ably higher but still are reduced proportional to the time of ageing.

CO_2 has a considerable affect on CK life even at room temperature. The
effect of CO_2 on ageing at 80°C. is considerable and more of what we might
term "permanent" ageing results. We have not run chromate analysis on these
yet, but it can be presumed that more reduction occurred.

Mustard:

A wide variety of preadsorptions were made on CWS carbon before mustard
sorption. Mineral oil, cresols, and Drifilm all gave increased desorption
of mustard. M-5 ointment absorbed on CWS carbon from acetone gave a consider-
able increase in desorption. It is, of course, possible (as usual) that the
oxidizable S used for analysis might be something other than mustard.

Attempted high temperature sulfonation of CWS carbons at 150, 200, 250 and 300°C. gave results showing little decrease in initial desorption rates but considerably reduced rates later for 200 and 250°C. sulfonations. These may be interesting enough to check further.

We found that we could get total chlorides by oxidation of the whole samples, and the mustard content on both carbons and ion exchange resins was checked. It was found in the latter case that only about 10% of the weight increase was mustard. These materials still show low desorption rates but the initial "H" concentration is too low to make them of any interest.

Chlorination at 400°C. had little effect on desorption and the use of pre-activated carbon after sulfonation gave very poor results. It was hoped that since this material has fairly high surface area and considerable hydrogen that it would sulfonate.

Dowex Ion Exchange Resin No. 50-x8 picked up more "H" and it had more desorption than IR-120. These can not be compared on initial "H" concentrations since we only have chloride analysis on the latter.

A method of analysis for "H" in solution by DB3 was worked out. The concentration in our water desorption experiments never is high enough for accurate analysis. A hydrolysis curve was made. The results were very questionable below roughly 10 mg./1.

Calculations were made to show the maximum "H" concentration obtainable for the consecutive reactions of desorption and hydrolysis. It was assumed that both reactions were first order. If the initial concentration of "H" is taken as that desorbed at very long times, a reasonable first order curve resulted. For most of the systems where from 10 to 30 grams of H/100 g. of C were adsorbed, the maximum concentration of "H" would be around 3 mg./1. using 1 g. C/200 g. of H_2O and this would be reached in about 40 minutes. For very high loadings, "H" concentration would get to 100 mg./1.

CONCLUSIONS:

1. The reversible ageing of ASC Whetlerite is a process of low activation energy and is probably physical rather than chemical.

2. Carbon dioxide, even at room temperature, has a considerable affect on CK life. Ageing, as already noted, is considerably higher in a CO_2 atmosphere and though there is reversibility on drying, recovery shows more "permanent" ageing results.

3. So-called reversible ageing is more or less proportional to permanent ageing.

4. No good solutions are as yet apparent for the prevention of mustard desorption from CWS carbon by water.

5. Most additives to the carbon increase desorption. Chemical treatments with H_2 or acids will decrease the rate but not sufficiently to be of much interest.

RESULTS:

The very large effect of drying after ageing was further investigated. For the want of better terms we have called the loss in CK life which is restored by drying, "reversible ageing" and the rest "permanent ageing". It is desirable to understand the "reversible ageing" since it is, (1) the largest effect, and (2) though easily restored in a kitchen oven or the like, it may otherwise be the hardest to counteract. At any rate, factors that influence one form may not influence the other.

The following tests were made to determine how easily reversible ageing can be reversed by room temperature drying with partially humid air, what effect water soluble components may have on the ageing, and what effect very severe continued ageing has.

The following tables show the results.

In addition, a somewhat similar series was run in which equilibration at 80% RH was made with CO_2, part of this material aged, part redried and CK tests made on all three materials.

Plant ASC Whetlerite was used in all these cases.

All the data is summarized in Table VIII. Weights are shown here and this shows that reversible ageing is not due to water content.

TABLE I

EFFECT OF TEMPERATURE OF DRYING AGED SAMPLES

A sample of plant production ASC was equilibrated and aged for 24 hours at 80°. The sample was split and dried under various conditions and then re-equilibrated.

CK Life in Minutes of 6 cm. Bed Depth	CK Life min.
Initial Life	237
Aged 24 hours at 80°	56
Aged 24 hours at 80° and partially dried in a 28% RH air stream for 18 hours at room temp.	129
Aged 24 hours at 80°, dried 3 hours at 105° and re-equilibrated	154
Aged 24 hours at 80°, dried 3 hours at 150° and re-equilibrated	154

TABLE II

EFFECT OF LENGTH OF AGEING TIME UPON RECOVERY OF CK LIFE AFTER REDRYING

Samples of plant production ASC were equilibrated and aged at
80° for various lengths of time. The samples were then split
and one-half of each was dried for 3 hours at 150° and then
re-equilibrated.

CK Life in Minutes for 6 cm. Bed Depth

	CK Life - Minutes	
		Redried & Re-Equil.
Initial	237	-
Aged 80° for 24 hours	56	154
Aged 80° for 48 hours	18	103
Aged 80° for 120 hours	17	74

TABLE III

EXPOSURE TO 80% RH AIR AFTER AGEING

A sample of plant production ASC was equilibrated at 80% RH
and then aged 24 hours at 80°. After ageing, the sample was
replaced on equilibrator and 80% RH air passed through for
varying times.

CK Life in Minutes for 6 cm. Bed Depth	CK Life min.
Aged 24 hours at 80°	36.6
Aged 24 hours at 80°, replaced on equilibrator for 24 hours	40.2
Aged 24 hours at 80°, replaced on equilibrator for 50 hours	45.0
Aged 24 hours at 80°, replaced on equilibrator for 120 hours	50.6

TABLE IV

ASC WASHED WITH WATER AND REDRIED

A sample of plant production ASC was washed with two liters water over a period of three hours. (Approximately 10% of the CrO_3 was washed off). Sample was dried three hours at 150° and equilibrated.

	CK Life - Minutes	
	Unwashed	Washed
Initial	237	163
Aged 24 hours at 80°	37	12

TABLE V

EQUILIBRATION AND AGEING IN CO_2

A sample of plant production ASC was equilibrated at 80% RH in a CO_2 atmosphere. The aged sample was sealed while on the equilibrator and placed in the oven.

CK Life in Minutes of 6 cm. Bed Depth

	CK Life - Minutes	
	Equilibrated with	
	80% RH Air	80% RH CO_2
Initial Life	237	144
Aged 24 hours at 80°	56	19
Aged 24 hours at 80°, redried 3 hours at 150°, re-equilibrated	154	117

TABLE VI

MISCELLANEOUS TESTS

A sample of plant production ASC was soaked in 12% chromic acid for 30 minutes, drained and dried for 3 hours at 150°. Sample was equilibrated at 80% RH.

	CK Life - Minutes
Initial Life 6 cm. depth	253
Aged 24 hours at 80°	33

A sample of plant ASC was equilibrated at 97% RH and tested at 97%.

		CK Life - Minutes
Initial Life	4 cm.	88
	6 cm.	216

TABLE VII

CK TUBE TESTS

The following tube tests were run at 4.00 mg. CK per liter, 1.56 liters per minute.
Tube cross-section equals 2.77 sq. cm. All tests run at 80-80 RH except where noted.
All tests were run on plant production ASC.

	Bed Depth cm.	Equil. Weight g.	Corrected Life min.	mg. CK	mg. CK per Gram Equil. Weight	Net Weight Change mg.
Equilibrated in CO_2						
Initial	6	11.2908	144.1	899	79.6	- 225.3
Aged 24 hours at 80°	6	11.2609	18.6	116	10.3	-
Aged 24 hours at 80°, Redried 150°,	6	11.2070	116.5	727	64.9	- 66.0
and Re-equilibrated in air.						
Aged 80° for 24 hours	6	11.1504	36.6	228	24.5	+ 113.8
Aged 80° for 48 hours	6	11.2697	18.1	113	10.0	-
Aged 80° for 120 hours	6	10.8330	16.7	104	9.6	-
Aged 80° for 48 hours, dried 150°, Re-equil.	6	11.1539	102.7	641	57.5	- 45.1
Aged 80° for 120 hours, dried 150°, Re-equil.	6	11.1602	73.6	459	41.1	- 115.7
Aged 80° for 24 hours placed in 80% RH						
air stream for, 24 hours	6	11.3452	40.2	251	22.1	- 64.8
50 hours	6	11.2108	45.0	280	25.0	- 59.7
120 hours	6	11.3703	50.6	316	27.8	- 135.8
Aged 80° for 24 hours dried at room temp. in						
28% RH air stream then re-equil. to 80%	6	11.2502	129.2	806	71.6	- 110.6
Equil. 97% RH tested 97% RH						
Initial	4	7.8200	88.3	551	70.5	- 67.7
Initial	6	11.5194	216.1	1348	117.0	- 91.4
Dipped in 12% chromic acid, dried 150°,						
Equilibrated Initial	6	12.4351	253.4	1581	127.1	+ 57.0
Aged 24 hours at 80°	3	12.4763	32.0	203	16.3	+ 40.8
Aged 24 hours at 80°, dried 3 hours 105°						
Re-equilibrated	6	11.2815	153.6	958	84.9	- 82.8
Aged 24 hours at 80°, dried 3 hours 150°						
Re-equilibrated	6	11.3411	154.0	961	84.7	- 91.5
Equil 80% Initial Life	6	11.1584	237.0	1479	131.8	+ 45.8
Aged 80° for 24 hours	6	11.1888	55.6	347	31.0	+ 101.5
Sample washed with 2 liters water						
Approx. 10% of the Cr removed, dried, equil.	6	11.5128	163.4	1020	88.6	- 95.3
Aged 24 hours at 80°	6	11.2358	12.0	75	6.7	-

Mustard:

Procedure:

A. Treatment of CWS Carbon before Adsorption of Mustard:

1. CWS carbon was dipped in 20% oleum solution and heated to temperatures of 150°C., 200°C., 250°C., 260°C., and 300°C. Samples were then drowned in ice, filtered, and dried overnight in forced draft oven at 150°C.

2. Samples of CWS carbon were placed in a vertical tubular furnace at a temperature of 400°C. and Cl_2 passed over it for 3 hours at 1 l./min. flow rate.

3. Samples of activator feedstock (devolatilized coal before activating) were dipped in solutions of oleum and chlorosulfonic acid, heated to 150°C. for 30 minutes, drowned, filtered and dried at 150°C. overnight.

4. Samples of CWS carbon were dipped in solutions of M-5 ointment in acetone and then air dried.

5. Samples of CWS carbon were dipped in Drifilm (General Electric) and then dried in forced draft oven overnight at 105°C.

B. Treatment of Other Adsorbents before Adsorption of Mustard:

1. Dow Resin No. 50-x8 was dried in oven overnight at 105°C. and then tightly bottled prior to mustard adsorption.

2. Linde's Molecular Sieves Type 5A was also dried overnight at 105°C. prior to use with mustard.

3. A sample of Resin IR-120 was dipped in NaCl solution and dried prior to adsorption of mustard.

C. Adsorption of Mustard by Various Samples:

1. The same procedure was initiated as reported, i.e., samples were placed in desiccator over a pool of mustard and the desiccator evacuated by a water aspirator. The amount of mustard adsorbed was determined by periodic weighing.

2. A desiccator filled with silica gel and evacuated by means of an oil vacuum pump was used in order to prevent the adsorption of water by the samples.

D. Use of the DB3 Method for Determination of Mustard in Aqueous Solution:

A sample of CWS carbon which had adsorbed a known amount of mustard was placed in 400 ml. of water and agitated. Samples were taken at measured intervals and the total mustard determined by coulometric titration and by a revised procedure using DB3 reagent. The procedure was as follows:

1. 1 ml. standard or sample   ) mixed, heated in boiling water
   5 ml. DB3 reagent   ) for 5 minutes and then cooled
   3 ml. H_2O) in cool water for 2-3 minutes.

2. Add 1 ml. acetone and 1 ml. piperidine and mix.

3. Read at 575 max. on spectrophotometer against distilled water.

4. Run blank using 1 ml. phthalate instead of sample.

A hydrolysis curve for mustard was determined by DB3 method by preparing a known standard of mustard in acetone and diluting to 1000 ml. Samples were then taken at measured intervals and the above DB3 method followed.

E. Determination of Mustard Content by Chloride and Sulfur Analysis:

Samples of resins and carbons which were thought to have a known amount of mustard adsorbed (determined by weight pick-up) were analysed for Cl and S content.

TABLE VIII

DESORPTION OF MUSTARD FROM CARBON

(Dipped in 20% Oleum at 150°C.)

CWS Carbon - 2.0064 g.
Mustard   - 0.4649 g.   H/C = 23.2

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	49.2	10.6
2	60	60.0	12.9
3	90	67.9	14.6
4	120	74.2	16.0
5	150	76.1	16.4
6	180	75.1	16.1
7	260	78.8	17.0
8	280	79.8	17.2
9	340	81.2	17.5
10	400	96.7	20.8
11	460	92.3	19.8
12	490	93.2	20.1
13	1455	126.4	27.2
14	1480	125.0	26.9
15	1510	125.3	27.0

TABLE IX

DESORPTION OF MUSTARD FROM CARBON

(Dipped in 20% Oleum at 150°C.)

CWS Carbon - 2.0152 g.
Mustard - 0.6342 g.   H/C - 31.5

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	38.92	6.13
2	90	70.2	11.1
3	120	76.2	12.1
4	180	89.6	14.1
5	240	92.8	15.8
6	1200	155.1	24.5
7	1260	165.4	26.1
8	1320	161.1	25.4

TABLE X

DESORPTION OF MUSTARD FROM CARBON

(Dipped in 20% Oleum and Held at 150°C.)

Carbon - 1.686 g.
Wt. addition due - 0.328 g.
  to sulfonation
Mustard - 0.6921 g.   H/C - 41.2

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	66.4	9.6
2	90	86.3	12.5
3	120	97.3	14.0
4	150	98.9	14.3
5	210	108.5	15.7
6	270	113.3	1...
7	330	119.4	17.3

TABLE XI

DESORPTION OF MUSTARD FROM CARBON

(Carbon Dipped in 20% Oleum at 200°C.)

Carbon   - 1.718 g.
Mustard   - 0.4423 g.   H/C = 25.8
Wt. addition due - 0.307 g.
  to sulfonation

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	11.9	2.7
2	50	12.8	2.9
3	80	15.4	3.5
4	110	16.0	3.6
5	140	18.1	4.1
6	170	19.0	4.3
7	200	21.7	4.9
8	260	35.3	8.0
9	290	33.5	7.6
10	350	32.9	7.5

TABLE XII

DESORPTION OF MUSTARD FROM CARBON

(Carbon Dipped in 20% Oleum at 250°C.)

Carbon   - 1.733 g.
Wt. addition due
  to sulfonation - 0.313 g.
Mustard   - 0.4090 g.   H/C = 23.6

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	7.7	1.88
2	60	11.6	2.83
3	150	15.6	3.81
4	210	16.1	3.93
5	270	18.2	4.4
6	330	19.0	4.6
7	1320	29.8	7.3
8	1380	31.1	7.6
9	1440	30.4	7.4
10	1500	30.5	7.4

TABLE XIII

DESORPTION OF MUSTARD FROM CARBON

(Carbon Dipped in 20% Oleum at 260°C.)

Carbon	- 1.637 g.	
Wt. addition due to sulfonation	- 0.379 g.	
Mustard	- 0.4489 g.	H/C = 27.5

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	10.0	2.2
2	120	16.1	3.6
3	180	17.9	4.0
4	240	19.3	4.3
5	300	21.2	4.7
6	360	22.8	5.1
7	1350	36.8	8.2
8	1410	37.5	8.3
9	1470	39.5	8.8

TABLE XIV

DESORPTION OF MUSTARD FROM CARBON

(Carbon Dipped in 20% Oleum Solution; Heated to 300°C.)

Carbon	- 2.0091 g.	
Mustard	- 0.4720 g.	H/C = 23.5

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	28.5	6.04
2	60	37.8	8.0
3	120	47.6	10.1
4	150	51.3	10.9
5	180	52.4	11.1
6	240	58.3	12.4
7	270	61.2	13.0
8	300	65.7	13.9
9	330	74.8	15.9
10	360	64.8	13.8

EFFECT OF VARIOUS OLEUM TREATMENTS
ON
MUSTARD DESORPTION
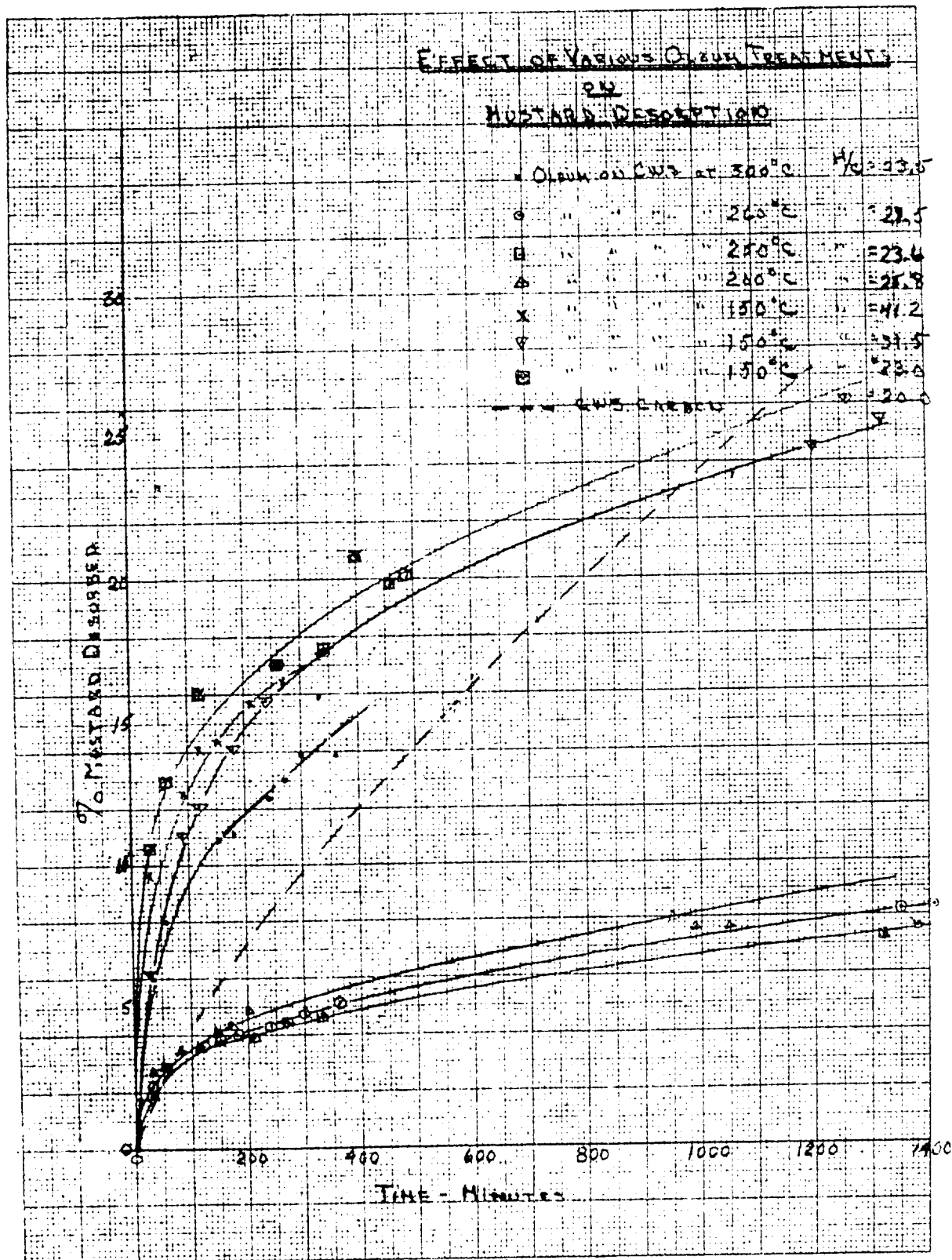
TABLE XV

DESORPTION OF MUSTARD FROM CARBON

(CWS Carbon Chlorinated at 400°C.)

Carbon - 2.0133 g.
Mustard - 0.6387 g.   H/C = 31.7

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	75.0	11.75
2	90	113.1	17.7
3	120	143.5	22.5
4	150	150.1	23.5
5	180	153.5	24.1
6	210	161.3	25.3
7	1175	250.1	39.2
8	1205	303.7	47.6

TABLE XVI

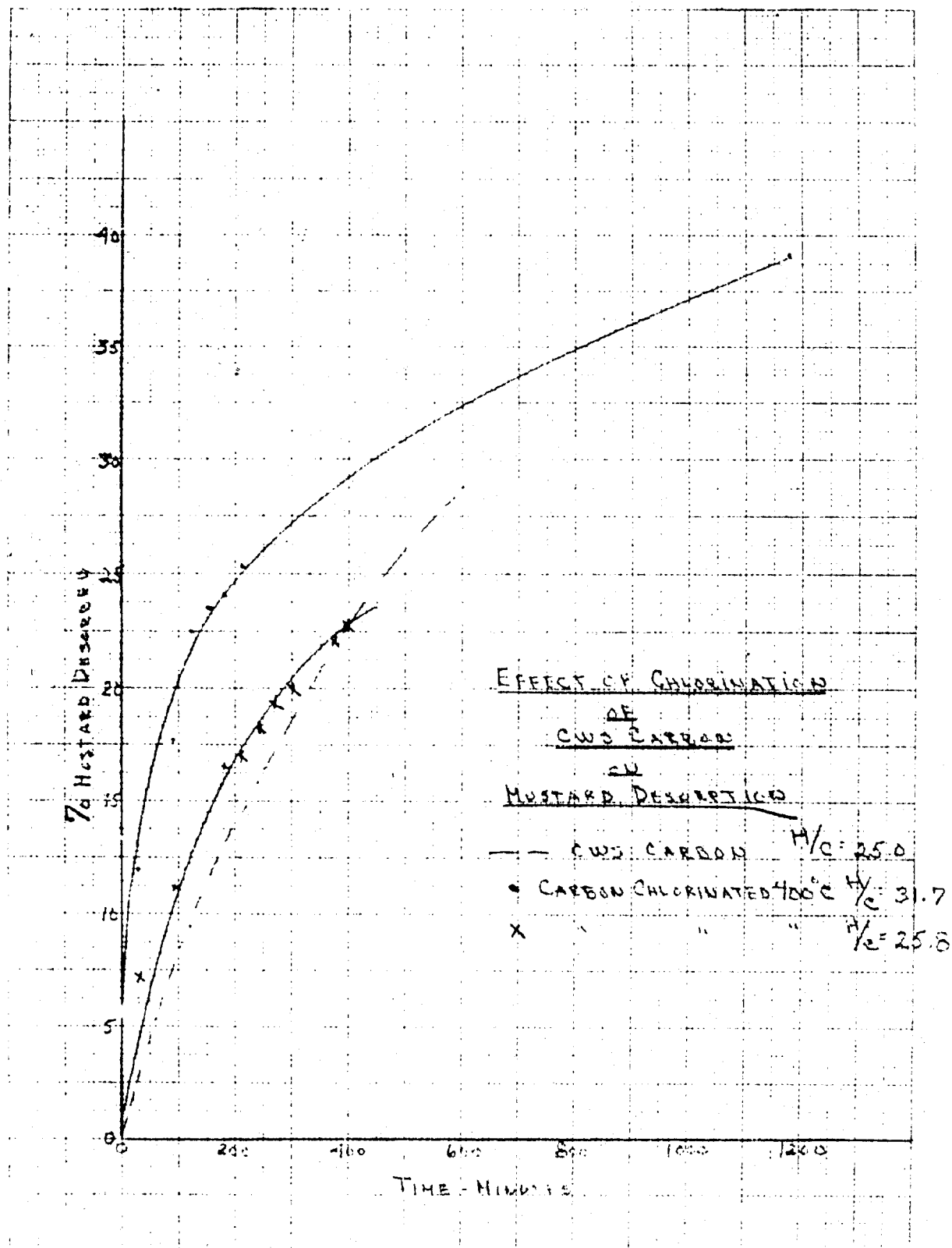### DESORPTION OF MUSTARD FROM CARBON

(CWS Carbon Chlorinated at 400°C.)

Carbon - 2.0090 g.
Mustard - 0.5173 g.   H/C = 25.8

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	37.1	7.18
2	90	57.5	11.1
3	180	85.7	16.6
4	210	87.4	16.9
5	240	94.0	18.2
6	270	100.0	19.4
7	300	103.0	19.9
8	360	114.1	22.1
9	390	119.4	23.1

EFFECT OF CHLORINATION
OF
CWS CARBON
ON
MUSTARD DESORPTION

— — CWS CARBON $H/c = 25.0$
• CARBON CHLORINATED 400°C $H/c = 31.7$
×   "   "   "   " $H/c = 25.8$

% Mustard Desorbed (y-axis)
TIME - MINUTES (x-axis)

TABLE XVII

DESORPTION OF MUSTARD FROM CARBON

(Baker "A" Material Dipped in ClHSO₃)

Baker "A" - 2.1235 g.
Mustard - 0.1155 g.   H/C = 5.4

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	19.9	17.25
2	90	25.1	21.7
3	150	28.5	24.8
4	1125	57.5	49.8
5	1185	55.0	47.6
6	1245	53.1	46.0
7	1305	53.4	46.3
8	1425	52.6	45.5
9	1485	52.2	45.2
10	1605	54.1	46.8

TABLE XVIII

DESORPTION OF MUSTARD FROM CARBON

(Activator Feed Stock Dipped in 20% Oleum Solution)

Activator Feed Stock - 2.0264 g.
Mustard - 0.1606 g.   H/C = 7.93

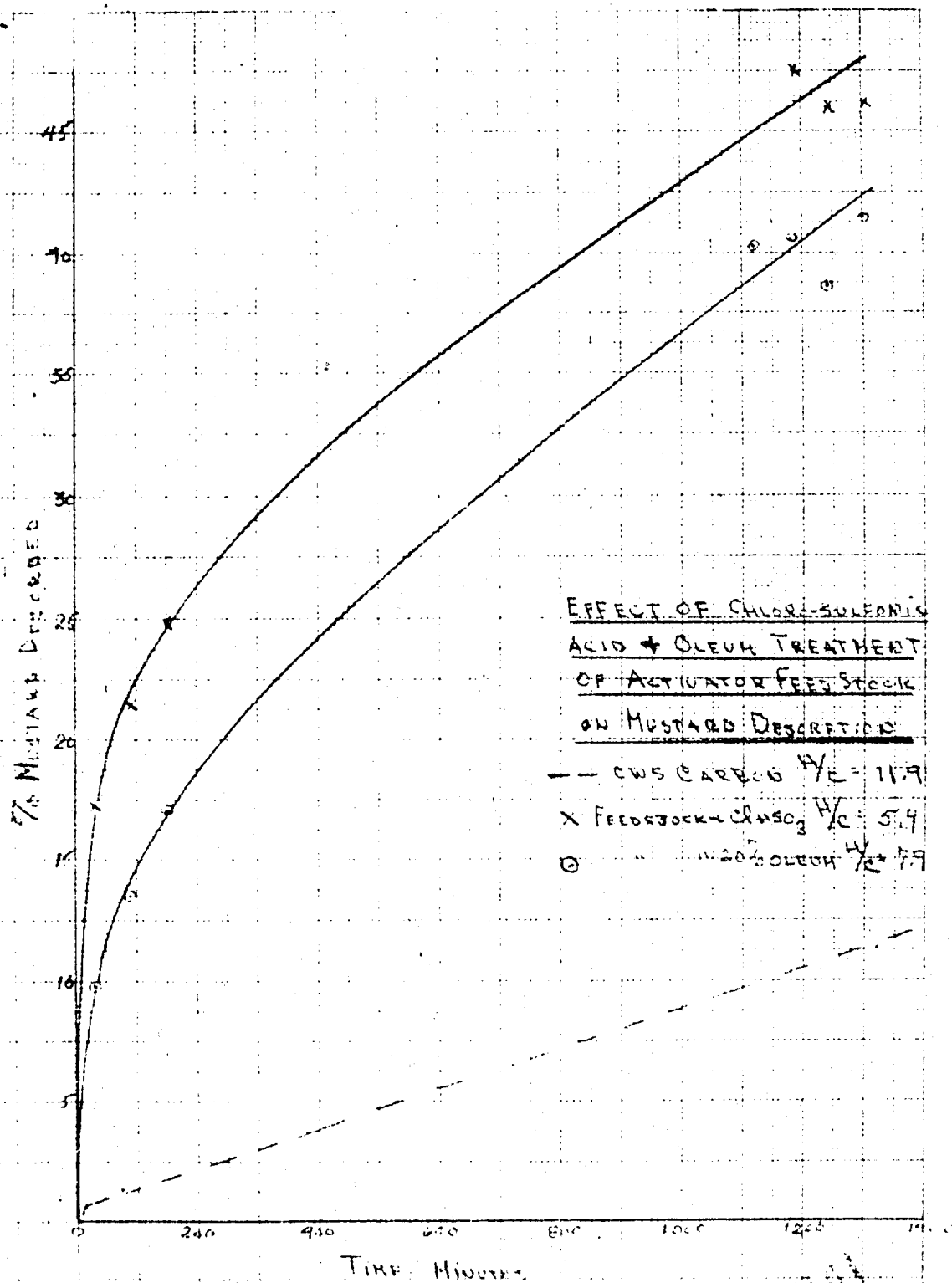| Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	15.7	9.8
2	90	21.6	13.5
3	150	27.4	17.1
4	1120	64.8	40.3
5	1180	64.9	40.5
6	1240	61.8	38.6
7	1300	66.4	41.4
8	1420	70.5	43.9
9	1480	65.2	40.7
10	1540	66.7	41.6

DESORPTION OF MUSTARD FROM CARBON

CWS Carbon - 2.0110 g.
Mustard - 0.2405 g.   H/C = 11.9

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	15	1.4	0.58
2	45	2.3	0.96
3	75	3.1	1.3
4	105	6.1	2.5
5	135	3.7	1.6
6	165	4.7	2.0
7	195	5.4	2.3
8	225	5.9	2.5
9	1260	26.3	10.9
10	1290	25.0	10.4
11	1320	27.3	11.3
12	1350	28.3	11.8

EFFECT OF CHLORI-SULFONIC
ACID & OLEUM TREATMENT
OF ACTIVATOR FEED STOCK
ON MUSTARD DESORPTION

— CWS CARBON $H/c = 11.9$
X FEEDSTOCK — $ClHSO_3$ $H/c = 5.4$
⊙ " — 20% OLEUM $H/c = 7.9$

TABLE XX

DESORPTION OF MUSTARD FROM CWS CARBON

(Carbon Impregnated with M5 Ointment in Acetone Solution)

Carbon — 1.4402 g.
M5 — 0.562 g.
Mustard — 0.1602 g.   H/C = 11.1

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	22.8	14.2
2	90	40.5	25.3
3	150	52.7	32.9
4	210	42.9	26.8
5	1200	143.9	89.8
6	1260	147.8	92.3
7	1320	147.4	92.1
8	1350	145.7	91.0

TABLE XXI

DESORPTION OF MUSTARD FROM CWS CARBON

(Carbon Impregnated with M5 Ointment in 50% Acetone Solution)

Carbon — 2.0047 g.
M5 — 0.7042 g.
Mustard — 0.2787 g.   H/C = 13.9

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	35.2	12.6
2	90	78.1	28.0
3	150	92.6	33.2
4	210	116.5	41.7
5	1200	242.6	87.0
6	1260	243.2	87.2
7	1320	240.0	86.2

TABLE XXII

DESORPTION OF MUSTARD FROM CWS CARBON

(Carbon Dipped in General Electric Drifilm 81268)

Carbon - 0.913 g.
Drifilm - 1.097 g.
Mustard - 0.0840 g.   H/C = 9.2

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	19.0	22.6
2	60	22.2	26.4
3	90	26.7	31.8
4	120	29.8	35.5
5	150	31.3	37.3
6	180	33.6	39.8
7	210	36.5	43.2
8	3630	58.9	70.0
9	3660	47.6	56.6
10	3690	56.7	67.5
11	3750	61.4	73.2
12	3910	61.8	73.6
13	3870	58.6	69.7

TABLE XXIII

DESORPTION OF MUSTARD FROM DOW RESIN NO. 50-x8

Resin   - 2.0467 g.
Mustard - 0.7159 g.   H/R = 35.0

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	7.3	1.0
2	60	9.3	1.3
3	90	12.3	1.7
4	120	14.1	2.0
5	150	16.4	2.3
6	180	19.0	2.7
7[1]	2580	82.1	11.4
8	2625	85.3	12.0
9	2655	79.6	11.0

[1] Agitation stopped for 40 hours

TABLE XXIV

DESORPTION OF MUSTARD FROM DOW RESIN NO. 50-x8

Resin   - 2.0312 g.
Mustard - 0.2071 g.   H/R = 10.2

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	4.0	1.9
2	90	7.1	3.4
3	150	9.5	9.6
4	210	16.1	7.8
5	1200	44.0	21.3
6	1320	44.1	21.3
7	1380	49.7	24.1
8	1440	47.6	23.0

TABLE XXV

DESORPTION OF MUSTARD FROM MOLECULAR SIEVE TYPE 5A

Molecular Sieve - 2.0996 g.
Mustard   - 0.4171 g.   H/R = 19.9

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	23.3	5.6
2	60	27.1	6.5
3	150	24.5	5.9
4	180	25.7	6.2
5	240	25.8	6.2
6	300	27.1	6.5
7	360	28.2	6.8
8	1380	31.8	7.6
9	1440	31.4	7.5
10	1500	31.2	7.5

TABLE XXVI

DESORPTION OF MUSTARD FROM ION EXCHANGE RESIN

(IR-120 - NaCl Washed)

Resin   - 2.0467 g.
Mustard - 0.2369 g.

Sample No.	Time Min.	"H" Desorbed mg.	"H" Desorbed Wt. %
1	30	0.22	0.09
2	60	0.26	0.11
3	120	0.23	0.10
4	150	0.32	0.13
5	180	0.16	0.07
6	210	0.35	0.15

TABLE XXVII

DESORPTION OF MUSTARD FROM CWS CARBON[1]

Carbon - 2.0073 g.
Mustard - 0.7835 g.
H_2O - 400 ml.

Sample No.	Time Min.	("H" & "TDG") Desorbed (Coulometric Deter.) microgram/ml.	"H" Desorbed (DB3) microgram/ml
1	10	100	3.5
2	20	125	4.0
3	30	164.5	3.0
4	40	175	5.0
5	50	185	7.0
6	60	215	1.0
7	70	224	6.0
8	80	230	7.0
9	90	241	5.0

[1] Previous run abandoned due to sampling intervals being too large.

TABLE XXVIII

HYDROLYSIS OF MUSTARD BY DB3 DETERMINATION

(0.3317 gm./5 ml. Acetone/1000 ml. H_2O - 3 ml. Aliquot)

Time Min.	Optical Density	MCG/3 ml.	MCG/ml.
5	0.818	172	57.3
10	0.540	113	51.5
15	0.383	80	26.7
20	0.256	54	18.0
25	0.217	45	15.0
30	0.339	71	24.7
35	0.228	48	16.0
45	0.171	36	12.0
55	0.116	24	8.0
60	0.095	20	6.7
65	0.088	18.5	6.2
70	0.106	22	7.3
75	0.092	19	6.4
85	0.066	14	4.7
90	0.065	13.5	4.5
105	0.068	14.5	4.8
120	0.066	14	4.7

HYDROLYSIS OF MUSTARD

$C_0 = 331.7$ MICROGRAM / ML

TIME — MINUTES.

H^+ — MICROGRAM/ML
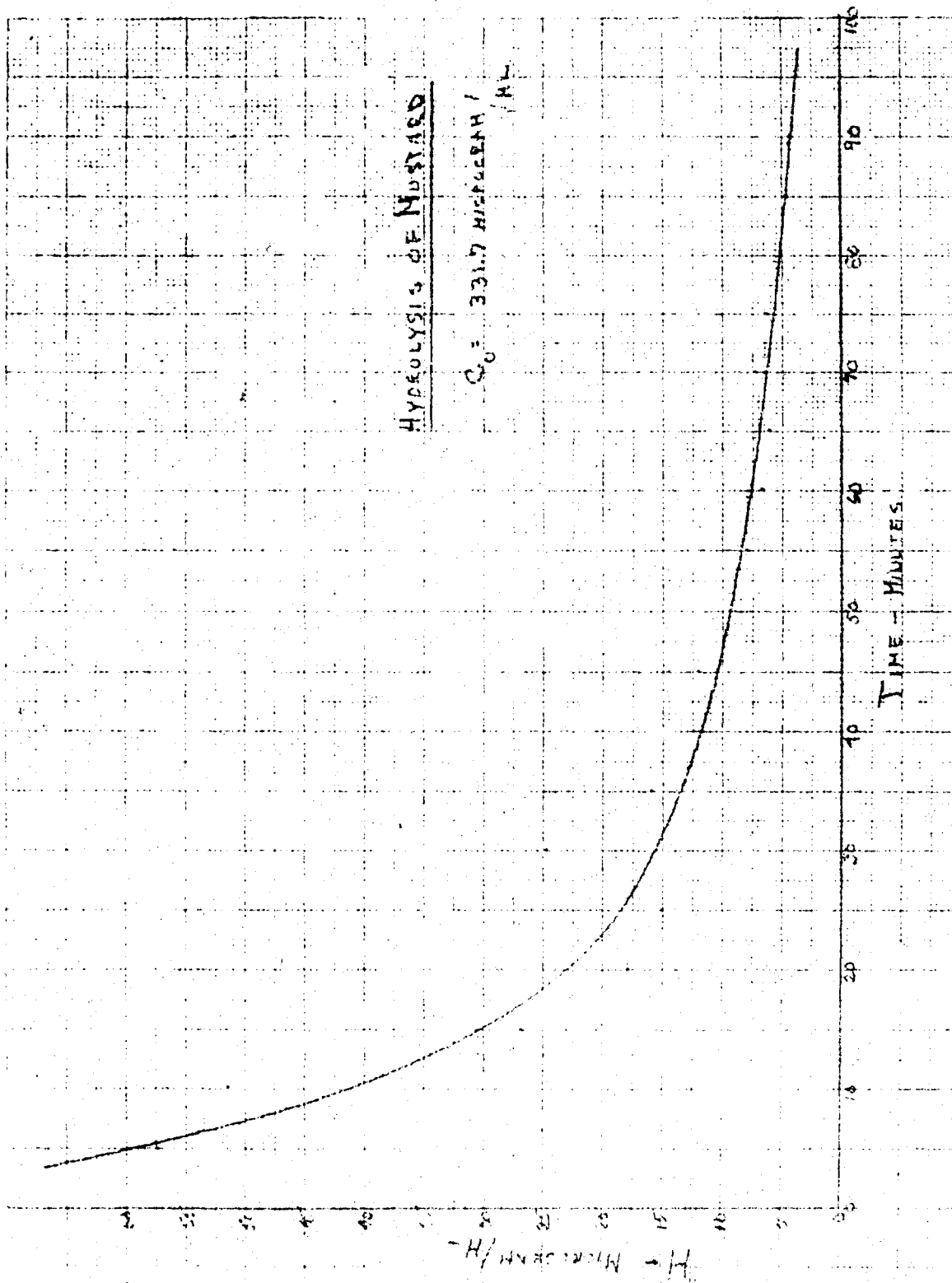
TABLE XXIX

DETERMINATION OF MUSTARD CONTENT

ON

VARIOUS SAMPLES

Sample	Cl⁻ Analysis g."H"/g. Sample	Sulfur Analysis	Weight Pickup g."H"/g. Sample
(1) Resin IR-120	0.0133 g.		0.148 g.
(2) Resin IR-120	0.0211 g.		0.139 g.
(3) CWS Carbon	0.148 g.	0.147 g.	0.224 g.
(4) CWS Carbon (Micronised)	0.369 g.	0.347 g.	0.35 g.

Samples (1), (2), and (3) - Adsorption conducted over mustard in a desiccator evacuated by water aspirator.

Sample (4) - Adsorption conducted over mustard and silica gel in a desiccator evacuated by vacuum pump.

DISCUSSION:

ASC Whetlerite:

Since drying material, aged at 80°C., 24 hours at 80% RH (RT), was reactivated
by essentially the same amount by drying at 150°C., 105°C. and RT with 28% RH
air, one would conclude that this reversible effect is due to a physical,
rather than a chemical, phenomena. At least the activation energy must be
quite low. Since chromate is apparently harder to leach (this is based on
the reasoning that it is very difficult to oxidize lower forms of Cr ion to
Cr^{+6}) the first thought is that some kind of pore plugging results. This
may or may not be due to formation of small amounts of hydrated Cr^{+3} ion.
Intermediate drying destroys the crust or gel allowing better penetration.
Room temperature drying is not very effective on Cr^{+3} hydrates and consider-
able doubt is thrown on this explanation. Precipitation of salts soluble
at high temperature and insoluble at low, might offer an explanation. This
effect would be much less dependent on the time at the high temperature.
The permanent ageing which we will label as due to Cr^{+6} reduction is in
part proportional to the reversible ageing and a combination of the above
effects might be responsible.

The effect of CO_2 ageing even at room temperature is very pronounced and
is not as reversible (at least after high temperature ageing). We shall
investigate this further.

Mustard:

While the IR-120 cation exchange resin still holds mustard apparently
irreversibly, it has been established that mustard pick-up is considerably
lower than previously thought so the results are not of direct practical
value.

Attempted sulfonation of activated carbon gave rather peculiar results.
Tests on ion exchange capacity will be run to determine an explanation of
the apparent maxima effect on sulfonating at 200 or 250°C. Initial mustard
desorption rates are the same which may be due to stoichiometric effects
(i.e., too high an "H" to SO_3H). As it stands we have not got any good
leads to producing irreversible adsorption of "H".

Attempts at analyzing for mustard as such in water by DB3 colorimetric analysis
gave little of value except that "H" was never present in reasonable quantities.
For this reason a series of calculations were made to predict "H" build-up.
It was found that log Co vs. 1/T plots were straight lines if a Co value
were picked as that possible to desorb by extrapolation of the desorption
curves. In order to simplify this somewhat, all the desorptions were assumed
first order and half lives were picked to be 1/2 the assumed Co (concentration
of H desorbed at finite times at the end of the desorption curve, usually
3000 minutes or more).

Thus

$$Carbon \cdot (ClC_2H_4)_2S \xrightarrow{K_1} (ClC_2H_4)_2S \; aqueous + H_2O \xrightarrow{K_2} (HOC_2H_4)_2S$$
$$+ 2HCl$$
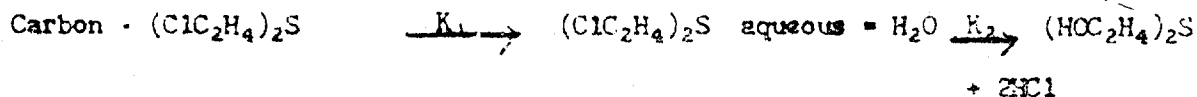
$$K_1 = \frac{0.693}{t \; 1/2} \qquad and \qquad K_2 = 0.1$$

The equation as developed by Glasstone and others for the maximum concentration of B in A → B → C in consecutive first order reactions is:

$$C_B \text{ max.} = A \frac{(K_2)}{(K_1)}^{\frac{K_2}{K_1 - K_2}}$$

and for the time at maximum C_B

$$t \text{ max.} = \frac{\ln K_1 / K_2}{K_1 - K_2}$$

where A = Co or initial concentration of A

To further simplify the calculations, K_1 was calculated for a series of half lives from 50 minutes to 1000 minutes. In general, half lives were of the order of 400 minutes assuming Co or A asabove.

TABLE XXX

CALCULATIONS FOR MAXIMUM MUSTARD CONCENTRATION

Adsorbent System	Nominal H/C in %	H/C used for Co %	Co or A mg./l.	t 1/2 min.	t max. min.	C "H" (max.) mg/l.
CWS Carbon	31	6.8	670	750	47	5.5
CWS Carbon	27.4	6.9	336	550	48	3.4
CWS Carbon	25	8.0	205	500	44	2.1
CWS Carbon micropulverized	22	5.1	250	450	43	2.9
CWS Carbon micropulverized	21.4	5.3	268	420	42	3.2
CWS Carbon H₂ treatment 400°	28.7	4.6	233	340	40	2.9
CWS Carbon 10% Acetic Acid	14	3.5	87	1000	50	0.6
CWS Carbon 10% HCl	19.4	1.3	65	500	44	.7
C Carbon 10% HNO₃	17.7	4.1	205	375	41	2.5
C Carbon + Ferric Oxalate	36.8	12.5	508	240	37	12
C Carbon + NH₄NO₃	40.2	17.5	850	270	38	17
ASC Whetlerite	42	20	1000	70	27	77
SiO₂	10	4	200	15	10	10
CWS Carbon	54	25	1238	70	26	103

The numbers in the above are obviously approximations at best and may even be misleading. They do show the difficulty in using any chemical method for determining mustard concentration in the water layer particularly when the DB3 method is not sensitive below 10 mg./liter. Since it is not known what concentrations are toxic to the skin and whether there is a threshold concentration, one hesitates to draw any conclusions. It is also true that in cases such as the sulfonated CWS carbons, the initial rate of desorption is considerably higher than later on and the reaction is not first order, except over a narrow range.

REPORT WRITTEN BY: _____

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